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Methane emissions from the 2015 Aliso Canyon blowout in Los Angeles, CA.

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In conclusion, pure H^- conduction was realized in the $\text{La}_{2-x-y}\text{Sr}_{x+y}\text{LiH}_{1-x+y}\text{O}_{3-y}$ system. The present success in the construction of an all-solid-state electrochemical cell exhibiting H^- diffusion confirms not only the capability of the oxyhydride to act as an H^- solid electrolyte but also the possibility of developing electrochemical solid devices based on H^- conduction.

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SUPPLEMENTARY MATERIALS

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GAS INFRASTRUCTURE

Methane emissions from the 2015 Aliso Canyon blowout in Los Angeles, CA

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Single-point failures of natural gas infrastructure can hamper methane emission control strategies designed to mitigate climate change. The 23 October 2015 blowout of a well connected to the Aliso Canyon underground storage facility in California resulted in a massive release of natural gas. Analysis of methane and ethane data from dozens of plume transects, collected during 13 research-aircraft flights between 7 November 2015 and 13 February 2016, shows atmospheric leak rates of up to 60 metric tons of methane and 4.5 metric tons of ethane per hour. At its peak, this blowout effectively doubled the methane emission rate of the entire Los Angeles basin and, in total, released 97,100 metric tons of methane to the atmosphere.

Large volumes of processed natural gas are stored underground to accommodate variability in energy demand on diurnal to seasonal time scales. Underground storage facilities constitute strategic gas reserves in many countries worldwide, with a volume equal to 10% of global annual consumption (1). Roughly 86% of stockpiled natural gas in the United States is stored at high pressure in depleted subsurface oil reservoirs (2). The Aliso Canyon storage facility, a depleted subsurface oil reservoir in the San Fernando Valley 40 km northwest of Los Angeles, CA, has a total capacity of 168 billion standard cubic feet (SCF) ($4.79 \times 10^9 \text{ m}^3$) at standard temperature and pressure, of which only 86 billion SCF ($2.5 \times 10^9 \text{ m}^3$; the “working capacity”) is routinely accessed for commercial use (2). It is the fourth largest facility of its kind in the United States, accounting for 2.1% of the total U.S. natural gas storage in 2014 (2). Processed natural gas is composed primarily of methane (CH_4), a powerful greenhouse gas, and ethane (C_2H_6), both of which can lead to background tropospheric ozone production; at sufficiently

high concentrations, natural gas leaks pose an explosion hazard and, if inhaled, can induce nausea, headaches, and impaired coordination. Exposure to odorants that are added to natural gas, which are typically sulfur-containing compounds such as tetrahydrothiophene [$(\text{CH}_2)_4\text{S}$] and 2-methylpropane-2-thiol [*t*-butyl mercaptan; $(\text{CH}_3)_3\text{CSH}$] can cause short-term loss of the sense of smell, headaches, and respiratory tract irritation. Major natural gas leaks therefore can have adverse impacts on climate, air quality, and human health.

On 23 October 2015, a major natural gas leak of indeterminate size was reported in the Aliso Canyon area and was later identified as originating from SS-25, one of 115 wells connected to the subsurface storage reservoir. The SS-25 well began oil production in 1954 and was converted to a gas storage well in 1973 (3). Seven unsuccessful attempts to close the leak have been reported. A relief well intercepted the leaking pipe at a depth of ~2600 m, below the subsurface breach; heavy fluid injection (a “bottom kill”) temporarily halted the leak on 11 February 2016, and cement injection sealed the well on 18 February 2016 (4).

We deployed a chemically instrumented Mooney aircraft in 13 flights from 7 November 2015 to 13 February 2016. We measured CH_4 and C_2H_6 to quantify the atmospheric leak rate and to assess air quality downwind of the leaking well (5). Ground-based whole-air sampling (WAS) with stainless steel canisters on 23 December 2015, followed by laboratory analysis, provided information on the chemical speciation of the leaking hydrocarbon mixture. We used the continuous airborne data and the ground-based WAS canister

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data to fingerprint the plume's chemical composition, quantify the atmospheric leak rate, and document trends in the leak rate over time.

The airborne chemical data showed the continuing transport on northerly winds of exceptionally high concentrations of CH_4 and C_2H_6 into the densely populated San Fernando Valley, a few kilometers south of the leaking well (Fig. 1). The plume C_2H_6 -to- CH_4 enhancement ratio (ER) derived from linear least-squares regression fits to the 23 December 2015 continuous airborne data is identical, within total uncertainties propagated by quadrature addition of errors (6), to the plume ER derived from WAS canister data taken at the surface on the same day (Fig. 2A).

The hydrocarbon composition of WAS canister samples taken at surface locations in the San Fernando Valley (Fig. 1) on 23 December 2015 (5) is consistent with a leak of pipeline-quality processed natural gas with a hydrocarbon composition of ~95% CH_4 , ~4% C_2H_6 , and ~0.3% propane (C_3H_8) (table S1). Plume enhancements of natural gas liquids (ethane, propane, and butanes) and condensates (pentanes and longer-chain hydrocarbons that are liquid at ambient temperature and pressure) were detected (table S1) and were probably responsible for reports of oily deposits on surfaces in downwind residential areas. Trace enhancements of benzene, toluene, ethylbenzene, and xylene isomers (the so-called BTEX compounds) were also detected at ratios of 0.001% or lower relative to CH_4 (table S1).

Benzene is a known human carcinogen (7); thus, population exposure to benzene from the Aliso Canyon leak has received particular attention. Composition data from the WAS canisters indicate a benzene-to- CH_4 enhancement ratio of $(5.2 \pm 0.1) \times 10^{-6}$ (uncertainties throughout are ± 1 SEM), which is broadly consistent with an ER of $\sim 7 \times 10^{-6}$ found in highly concentrated samples that were collected ~3 m downwind of the SS-25 well site (8). Together, these samples suggest minimal variation over time in the benzene composition of the leaking gas. Publicly available benzene data, reported in near-daily 12-hour air samples (9), were often below the detection limit of 1 nmol/mol [or 1 part per billion (ppb)] of the contract laboratories used for the analyses, but these data also show a relatively constant ER over time. Plume benzene enhancements can be estimated from the abundant CH_4 data by multiplying plume CH_4 enhancements by the benzene-to- CH_4 ER determined using the research-grade WAS canister samples. Sulfur-containing odorants were not measured, but concentrations above the odor threshold can be estimated similarly (Fig. 1) from observed CH_4 enhancements by assuming an industry-standard value of ~5 parts per million (ppm) of total odorant in processed natural gas (10).

Continuous airborne CH_4 and C_2H_6 data were taken on each flight between 11 AM and 3:30 PM (local time) with a resolution of 30 m along-track during repeated crosswind transects at multiple altitudes from 60 to 1400 m above ground. These data define the horizontal and vertical extent of

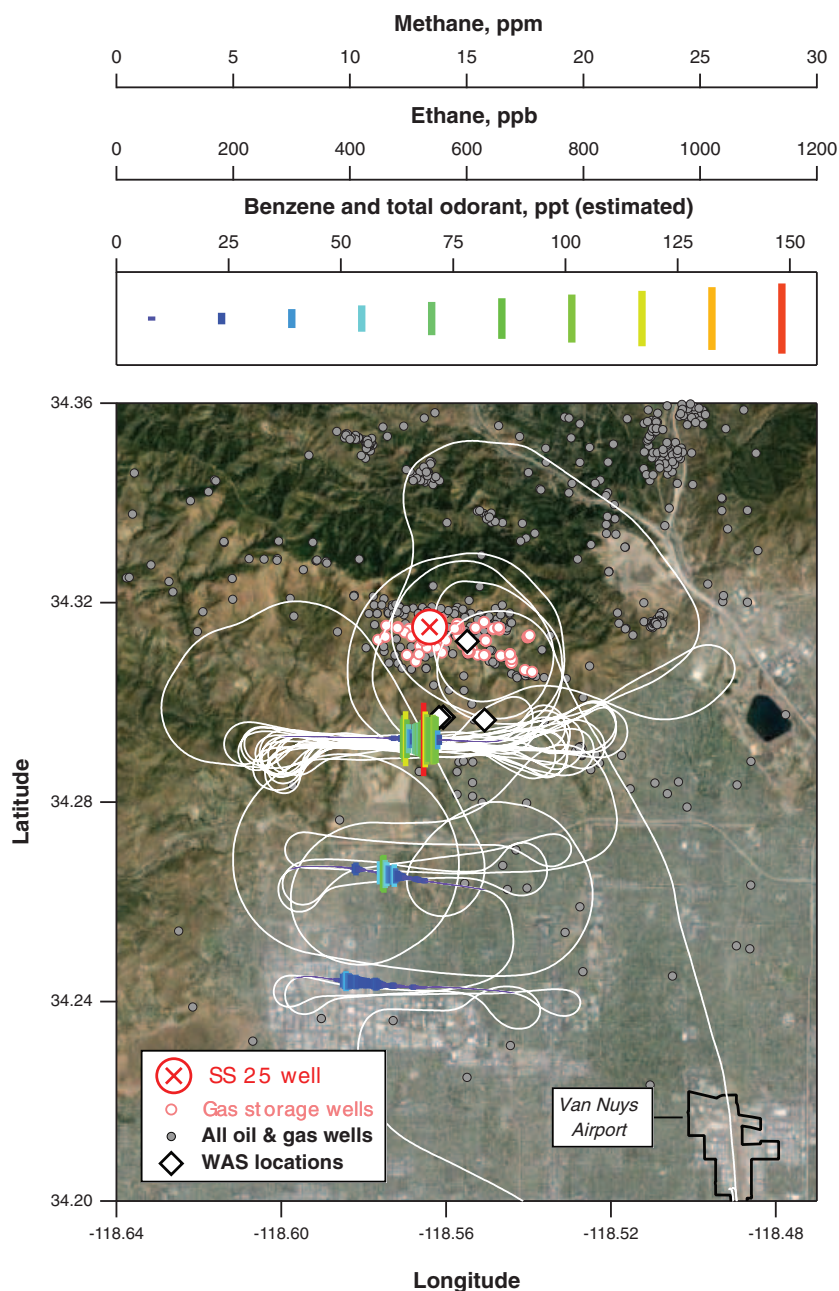


Fig. 1. Aliso Canyon gas plume transport into populated areas. Airborne chemical data illustrate plume transport into the San Fernando Valley; data from 10 November 2015 are shown. Plume enhancements above the local background (colored markers) from example transects are plotted along the flight track (white line) and can be scaled using the legends at top to yield measured CH_4 , measured C_2H_6 , estimated benzene based on the WAS benzene-to- CH_4 ER, and estimated total odorant (assuming 5 ppm in the leaking gas). Benzene and total odorant are in parts per trillion by volume (ppt).

the leaking natural gas plume on each flight (Fig. 1 and fig. S1). The flights provided highly spatially resolved data from which an atmospheric mass flux can be accurately calculated (11) within well-defined uncertainties (12). Plumes from nearby landfills have low concentrations of CH_4 , are easily identified by their lack of co-emitted C_2H_6 , and were eliminated from further analysis. Background levels of CH_4 and C_2H_6 were measured during aircraft transects on multiple flights immediately

upwind, confirming the SS-25 well as the dominant source of enhanced natural gas to the region. Operational restrictions on aircraft flight patterns were imposed by the elevated terrain at the leak site, the highly controlled airspace of the San Fernando Valley, and the proximity to approach corridors of the nearby Van Nuys Airport (Fig. 1). These restrictions were overcome by performing crosswind transects at multiple altitudes immediately downwind of the leak site,

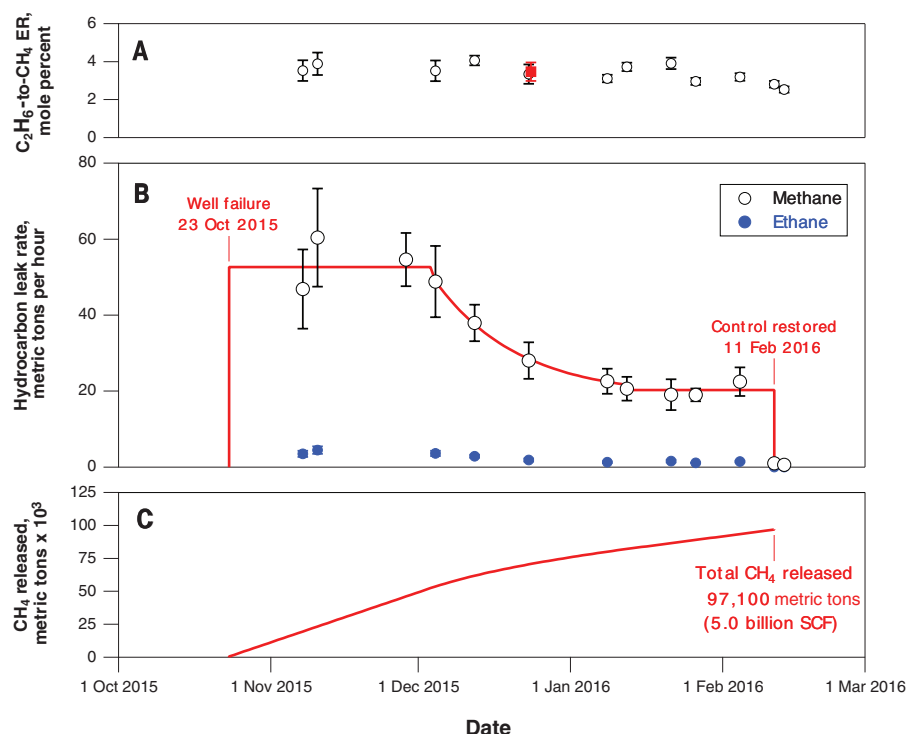


Fig. 2. Time series of the Aliso Canyon natural gas leak. (A) Plume C_2H_6 -to- CH_4 ERs from airborne measurements (open circles) and ground-based WAS measurements (red square). (B) Leak rates (in metric tons per hour) of CH_4 (open circles) and C_2H_6 (blue circles), determined from airborne measurements. The red line is a fit to the airborne CH_4 data, assuming an average leak rate from the blowout (day 0) to day 43, an exponential decrease between days 43 and 80, and an average leak rate thereafter to day 112, when control was restored. (C) The total amount of CH_4 released (in metric tons), calculated from the fit in (B). Error bars indicate ± 1 SEM.

which enabled accurate reconstruction of a vertical concentration profile, even before the plume had completely mixed throughout the full vertical extent of the atmospheric boundary layer (5).

The chemical data show that the airborne sampling captured the full vertical extent of the lofted plumes on each flight day (fig. S1). Atmospheric mass fluxes calculated from the chemical data from each transect collected downwind (5) suggest an average leak rate of 53 ± 3 metric tons of CH_4 and 3.9 ± 0.3 metric tons of C_2H_6 per hour for the first six weeks of the leak, decreasing thereafter (Fig. 2B and table S2). The decreasing trend, which began around the first week of December 2015 (Fig. 2B and table S2), is consistent with decreasing reservoir pressure in response to the withdrawal of gas through other storage wells connected to the subsurface reservoir, which was done in a deliberate effort to slow the leak (13). The lack of a decrease in the leak rate after the first week of January 2016 is consistent with the cessation of withdrawals to maintain a minimum working pressure in the reservoir, which supplied natural gas to customers in the greater Los Angeles basin throughout the leak duration.

These data demonstrate that the blowout of a single well in Aliso Canyon temporarily created the largest known anthropogenic point source of CH_4 in the United States (14), effectively doubling the leak rate of all other sources in the Los

Angeles basin combined (15, 16). Further, at its peak, this leak rate exceeded that of the next largest point source in the United States—an underground coal mine in Alabama—by over a factor of 2 (14) and was a factor of 10 larger than the CH_4 leak rate reported from the Total Elgin rig blowout in the North Sea in 2012 (17). The Aliso Canyon CH_4 leak rates were comparable to the total CH_4 emission rates of entire oil and gas production regions in the United States [e.g., the Barnett shale, 76 metric tons per hour (18); the Haynesville shale, 80 metric tons per hour (19); the Fayetteville shale, 39 metric tons per hour (19); and the northeastern Marcellus shale, 15 metric tons per hour (19)].

Our aircraft flights after the “bottom kill” confirmed the cessation of flow from the SS-25 well on 11 February 2016 and revealed a residual leak rate of <1 metric ton of CH_4 per hour (Fig. 2B and table S2), consistent with nonzero leak rates observed at other natural gas, oil, and petrochemical facilities nationwide (16, 18–24). These data show that over its 112-day duration, the Aliso Canyon natural gas leak released a total of 97,100 metric tons (5.0 billion SCF) of CH_4 (Fig. 2C) and 7300 metric tons (0.2 billion SCF) of C_2H_6 to the atmosphere, which is equal to 24% of the CH_4 and 56% of the C_2H_6 emitted each year from all other sources in the Los Angeles basin combined (16).

This CH_4 release is the second largest of its kind recorded in the United States, exceeded only by the 6 billion SCF (115,000 metric tons) of natural gas released in the 2004 collapse of an underground storage facility in Moss Bluff, TX, and greatly surpassing the 0.1 billion SCF (1900 metric tons) of natural gas leaked from an underground storage facility near Hutchinson, KS, in 2001 (25). Aliso Canyon will have the largest climate impact by far, however, given that an explosion and subsequent fire during the Moss Bluff release combusted most of the leaked CH_4 , immediately forming CO_2 . The total release from Aliso Canyon will substantially affect the State of California greenhouse gas (GHG) emission targets for the year (26) and is equivalent to the annual energy sector CH_4 emissions from medium-sized European Union nations (27). The radiative forcing from this amount of CH_4 , integrated over the next 100 years, is equal to that from the annual GHG emissions of 572,000 passenger cars in the United States (28). The volume of CH_4 released represents only 3% of the total capacity of the Aliso Canyon storage facility, raising the possibility of substantial additional emissions if the leaking SS-25 well had not been sealed, or if the remaining natural gas had not been withdrawn through other wells, before the reservoir was completely exhausted to the atmosphere.

The agreement reached at the 21st Conference of the Parties (COP21) to the UN Framework Convention on Climate Change (29) includes specific requirements for the Parties to account for anthropogenic GHG emissions with accuracy and completeness. In the post-COP21 world, rapid evaluation of episodic GHG release events, such as the Aliso Canyon blowout, will be an essential contribution to meeting these requirements.

Our analysis quantifies a massive CH_4 release using a rapid, direct, and repeatable method with known accuracy. As such, results from this method serve as reference values for less direct and timely estimates that use retrievals of surface (30, 31), airborne (32), and/or satellite remote sensing observations (33). For example, our airborne method offers a priori estimates of the Aliso Canyon leak rates that can be used for inverse modeling analysis of continuous in situ CH_4 monitoring data from fixed ground sites (15, 34). This incident highlights the utility of rapid-response airborne chemical sampling in providing an independent, time-critical, accurate, and spatially and temporally resolved leak rate, as well as in ascertaining the source location and plume chemical composition. Such information can help to document human exposure, formulate optimal well-control intervention strategies, quantify the efficacy of deliberate control measures, and assess the climate and air quality impacts of major unanticipated chemical releases to the atmosphere (35, 36).

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agencies. Data used in this report are posted at esrl.noaa.gov/csd/scientificaviation.

SUPPLEMENTARY MATERIALS

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BIOCHEMISTRY

Fine-tuning of a radical-based reaction by radical *S*-adenosyl-L-methionine tryptophan lyase

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The radical *S*-adenosyl-L-methionine tryptophan lyase NosL converts L-tryptophan into 3-methylindolic acid, which is a precursor in the synthesis of the thiopeptide antibiotic nosiheptide. Using electron paramagnetic resonance spectroscopy and multiple L-tryptophan isotopologues, we trapped and characterized radical intermediates that indicate a carboxyl fragment migration mechanism for NosL. This is in contrast to a proposed fragmentation-recombination mechanism that implied C α –C β bond cleavage of L-tryptophan. Although NosL resembles related tyrosine lyases, subtle substrate motions in its active site are responsible for a fine-tuned radical chemistry, which selects the C α –C bond for disruption. This mechanism highlights evolutionary adaptation to structural constraints in proteins as a route to alternative enzyme function.

Nosiheptide, produced by *Streptomyces actuosus*, is a highly modified, sulfur-rich, polythiazolyl macrocyclic peptide antibiotic (1). This compound exhibits highly potent activity against multidrug-resistant strains of several gram-positive pathogens (2–5). Originating from a 13-residue-long, ribosomally synthesized peptide, nosiheptide contains a central tetra-substituted pyridine ring, five thiazole rings, and an unusual indolic acid (6, 7). The latter is produced by the tryptophan lyase (NosL) enzyme, which converts L-tryptophan to the methylindolic acid (MIA) precursor that is subsequently inserted into the thiopeptide (8, 9). NosL

belongs to the radical *S*-adenosyl-L-methionine (SAM) protein superfamily, which uses a reduced [Fe₄S₄]⁺ cluster and SAM to initiate a 5'-deoxyadenosyl radical (5'-dA•)-based reaction (10). Homologous tyrosine lyases (CofH, ThiH, and HydG) cleave the C α –C β bond of tyrosine, producing a *p*-cresyl radical and dehydroglycine (DHG) (11–15).

Because of the prevalence of tyrosyl and tryptophanyl radicals in proteins, it was initially proposed that the H-atom abstraction from L-tyrosine and L-tryptophan by the highly reactive 5'-dA• should take place at the L-tyrosine phenol group and at the L-tryptophan indole nitrogen, respectively (9, 12, 14). However, a recent NosL structure in complex with L-tryptophan (16) indicates that the H-atom abstraction takes place at the amino nitrogen atom (Fig. 1A). Biochemical studies confirmed that this abstraction in NosL is the first step in the conversion of L-tryptophan into MIA. NosL can perform β -scissions from the amino-centered radical intermediate at either C α –C β or C α –C when using L-tryptophan analogs (17, 18). These observations suggest a relative propensity of NosL for substrate promiscuity that, combined with slight differences in

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Methane emissions from the 2015 Aliso Canyon blowout in Los Angeles, CA

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The magnitude of a major methane leak

The Aliso Canyon underground gas storage facility outside Los Angeles, CA, houses enormous natural gas reserves. One well at the site experienced a blowout in late October 2015 and began leaking gas until it was sealed in February 2016. Over the course of 13 flights in the region, Conley *et al.* sampled the air column and determined daily release rates of methane (a powerful greenhouse gas) and ethane throughout the leak. The methane release rates were nearly double that of the entire Los Angeles region combined. Thus, single vulnerabilities can have major implications for state and federal climate policy.

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